

## Supporting Information for

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**Title:** Secondary Organic Aerosol Formation from the Ozonolysis of Cycloalkenes and Related Compounds.

Number of pages in Supporting Information: 8

Number of figures in Supporting Information: 5

Number of Pages in Manuscript: 33

Number of Figures in Manuscript: 7

Number of Tables in Manuscript: 5

**Yield and Reaction Times.** Figure 1 shows examples of time series for ozone, hydrocarbon and particle volume concentration for each parent compound for experiments with initial hydrocarbon mixing ratio of approximately 200 ppb. The factors that govern the rate of the overall process include: (1) rate of the reaction between the hydrocarbon and ozone, which determines the rate at which the hydrocarbon is consumed and that at which gaseous secondary products form; (2) the amount of ozone consumed in the reaction, which provides information about the stoichiometry of the reaction; (3) the lag-time before the seed aerosol begins to grow, which provides information about the time required for secondary precursor concentrations to accumulate for partitioning from the gas to the particle phase to begin; and (4) the rate at which particle growth itself proceeds.

**Rate of Hydrocarbon Consumption.** The rate of hydrocarbon consumption is dependent on the initial hydrocarbon concentration, (Figure 2). Methylene cyclohexane and 3-methyl-1-cyclohexene display the slowest rates of consumption, and 1-methyl-1-cycloheptene, cyclopentene and 1-methyl-1-cyclopentene display the most rapid rates of consumption. The hydrocarbon decay rate is related to the rate constants for the reactions with ozone ( $k_{O_3}$ ) (Figure 3). Values of  $k_{O_3}$  for 1-methyl-1-cycloheptene and 3-methyl-1-cyclohexene are not currently available in the literature; the current data would suggest that these values are approximately  $600 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $55 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively (uncertainty of 30%). The value for 1-methyl-1-cycloheptene is lower than the value very recently measured by Cusick et al. (1) of  $930 \pm 29 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Ozone Consumption.** In all experiments, ozone was injected at the rate of  $5 \text{ L min}^{-1}$ , for the time required for the ozone concentration to reach three times the initial precursor

hydrocarbon concentration. For the 200 ppb initial mixing ratio experiments depicted in Figure 1, ozone was injected for 132 minutes. The theoretical concentration of ozone as a function of time in the absence of reaction is also shown in Figure 1 and can be compared with the actual ozone concentration. For methylene cyclohexane, very little of the ozone is consumed during the time when ozone is injected. In contrast, 1-methyl-1-cycloheptene displays the most rapid ozone consumption. The more slowly reacting compounds exhibit a decrease in ozone concentration after the ozone concentration peak, indicating that ozone consumption continues after injection.

**Particle Growth.** Figure 1 displays examples of the time series of particle growth for each compound. The initial shallow part of the growth curve reflects the time taken for the onset of particle growth, that is, the time required for sufficient build-up of secondary gaseous products before partitioning begins. The time required for the onset of particle growth is dependent on the rate of the hydrocarbon ozone reaction (Figure 4). For the fast reacting compounds, particles begin to be produced almost immediately after the start of ozone injection. The steep part of the particle growth curves shown in Figure 1 indicates the rate of particle growth, and this also differs between compounds. This rate is also dependent on initial hydrocarbon concentration (Figure 5).

The cycloalkenes and related compounds can be divided into three groups, primarily based on their ozone rate constant. The slow reacting compounds include methylene cyclohexene, 3-methyl-1-cyclohexene, and cyclohexene. The fast reacting compounds include 1-methyl-1-cycloheptene, cyclopentene, and 1-methyl-1-cyclopentene. The remaining compounds, cyclooctene, cycloheptene and 1-methyl-1-cyclohexene, show intermediate reaction rates. While the slow reacting compounds require more time for the onset of particle growth, consume less ozone than the fast reacting compounds and

exhibit a lower rate of particle growth, the yield of SOA is found to be independent of the hydrocarbon-ozone reaction rate.

(1)Cusick, R.; Arey, J.; Atkinson, R., *unpublished data*.

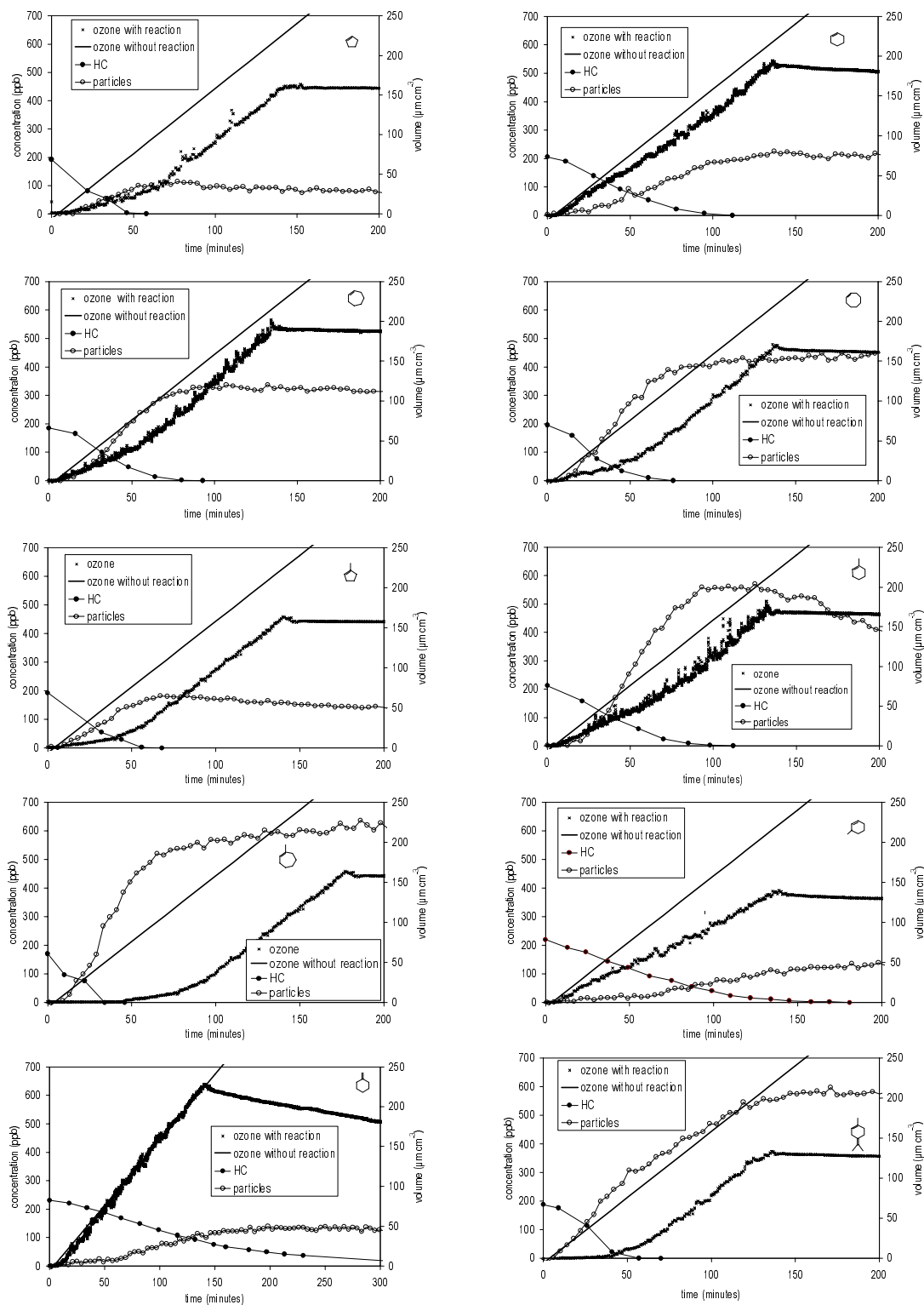


Figure 1. Time series for ozone, hydrocarbon and particle volume concentration for each compound measured in this study.

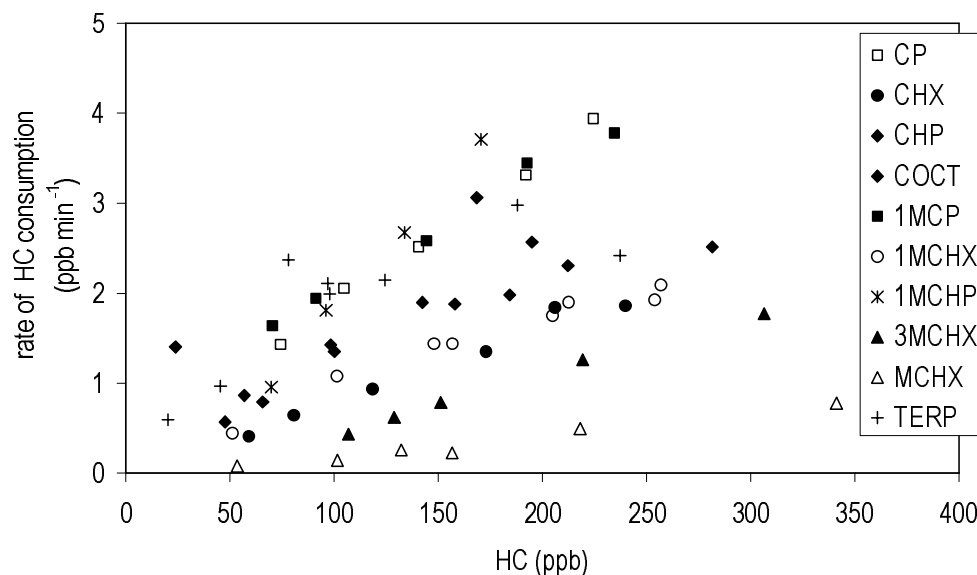


Figure 2. Rate of hydrocarbon consumption as a function of hydrocarbon concentration. CP is cyclopentene, CHX is cyclohexene, CHP is cycloheptene, COCT is cyclooctene, 1MCP is 1-methyl-1-cyclopentene, 1MCHX is 1-methyl-1-cyclohexene, 1MCHP is 1-methyl-1-cycloheptene, 3MCHX is 3-methyl-1-cyclohexene, MCHX is methylene cyclohexane and TERP is terpinolene.

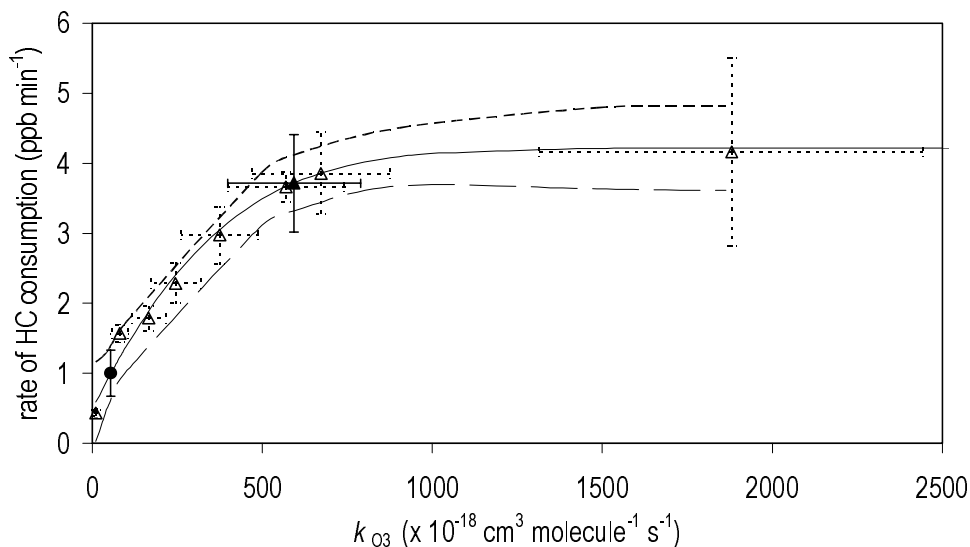


Figure 3. Rate of hydrocarbon consumption as a function of  $k_{O_3}$  based upon an initial hydrocarbon concentration of 200 ppb.  $k_{O_3}$  for 1-methyl-1-cycloheptene (solid triangle) is determined from this study to be  $600 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .  $k_{O_3}$  for 3-methyl-1-

cyclohexene (solid circle) is determined from this study to be  $55 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

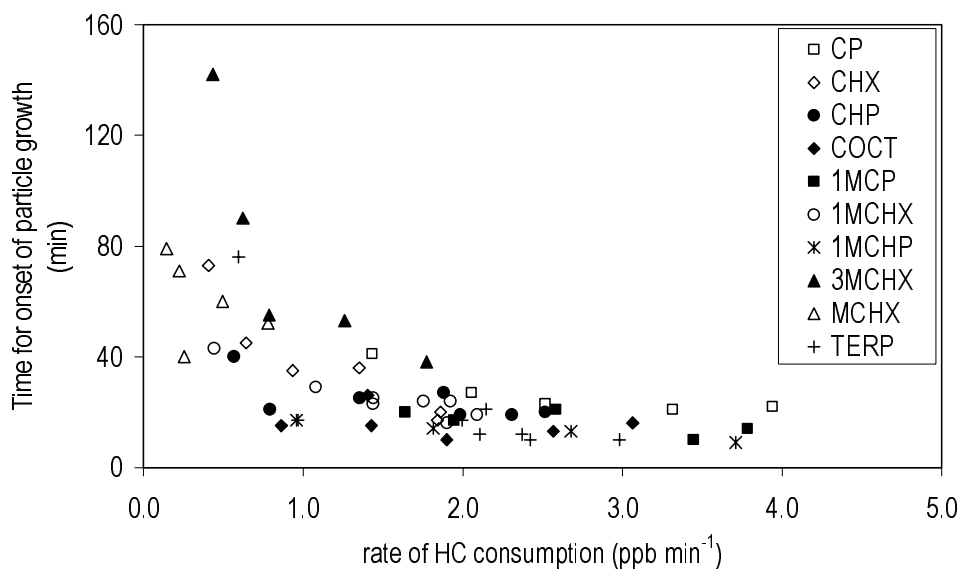


Figure 4. Time for the onset of particle growth as a function of  $k_{os}$ . See Figure 2 for legend description.

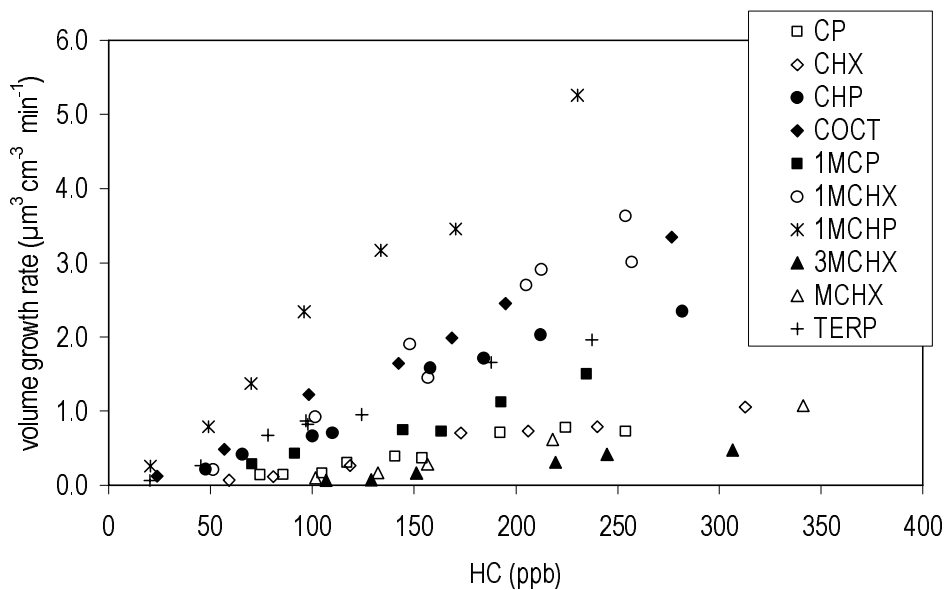


Figure 5. Rate of particle growth as a function of hydrocarbon concentration. See Figure 2 for legend description.

